



Next Generation Highly Conducting Organic Films Using Novel Donor-acceptor Molecules for Opto-electronic Applications

by Eric Forsythe, Jianmin Shi, and David Morton

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14. ABSTRACT <p>This two-year DRI is intended to address the Army's need for two-dimensional, conformal, large-area electronics by developing techniques that will lead to the printing of conducting organic materials as a primary build-block that will enable such low-cost, large area applications. In the first year, we worked on developing novel organic based molecules using the donor-acceptor design concepts and developing a more fundamental understanding of donor acceptor molecule stacking in order to guide future material designs. During the second year, the team will improve the ARL-08 materials and integrate these materials into flexible display with the Army's Flexible Display Center (FDC). The fundamental materials research will be integrated into diode devices to evaluate the device properties as a function of the material formations.</p>					
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1. Objective

The Army's transition to lightweight, rugged large area electronics will require novel materials and low-temperature processing on flexible substrates. The Army's need for two-dimensional (2-D) conformal large area electronics includes energy harvesting, information displays, and sensors. The results from this Director's Research Initiative (DRI) will lead to printing of conducting organic materials as a primary build-block that will enable these low-cost, large area applications.

Conducting organic materials are the primary components for Army applications that include large area electronics, solar cells, and information displays, as shown in figure 1. Neutral organic based thin films have equivalent charge mobility to intrinsic amorphous inorganic semiconductor thin films, where the transport is dominated by carrier hopping. However, inorganic semiconductors have a stable, well defined doping process to improve the charge mobility. Organic semiconductors, to date, have limited examples of doping the host materials to improve charge mobility (1, 2). The general program approach is to develop novel organic salts that are doped into a wide range of organic host materials. The organic salts will assist in the charge transfer to the host organic materials similar to doping an inorganic semiconductor. Conducting thin films will improve the device efficiency for a number of applications including photovoltaics, contact doping for thin-film transistors, light emitting devices, and ultimately conducting lines for large area flexible electronics.

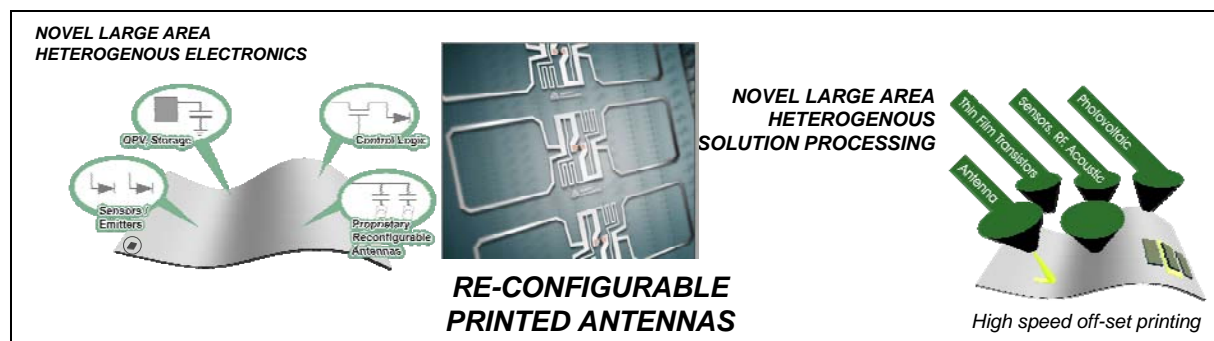


Figure 1. Application space for conducting organic materials.

Currently, researchers have demonstrated conducting small molecule based thin films using tetra-cyanoquinodimethane (TCNQ) doped into an aryl amine. In figure 1, TCNQ is doped at 1–5% into a specific aryl amine molecule where the TCNQ molecule oxidizes aryl amine. This approach is limited to TCNQ and the aryl amine for hole-transporting layers.

2. Approach

The novel salts that follow have been designed and synthesized at the U.S. Army Research Laboratory (ARL). The general concept developed in this DRI is illustrated in equation 1:



where $[\text{A}]^{-} [\text{B}]^{+}$ is a generic salt that can be thermally sublimed or processed in solution. This salt is then doped into a generic host organic material to demonstrate a conducting thin film.

3. Results

3.1 ARL-08 Hole-transporting Material

The novel hole-transporting material, ARL-08 doped with TCNQ per the design scheme illustrated in figure 1, has been compared to 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) as well as ARL-08 alone, a traditional hole-transporting small molecule used in commercial organic light emitting diode-based displays. In figure 2, the devices were fabricated as illustrated in the inset of figure 2a, with the hole-transporting layer fabricated on an indium tin oxide (ITO) transparent conducting electrode with a magnesium silver (Mg:Ag) top electrode. The positive voltage is applied to the ITO contact.

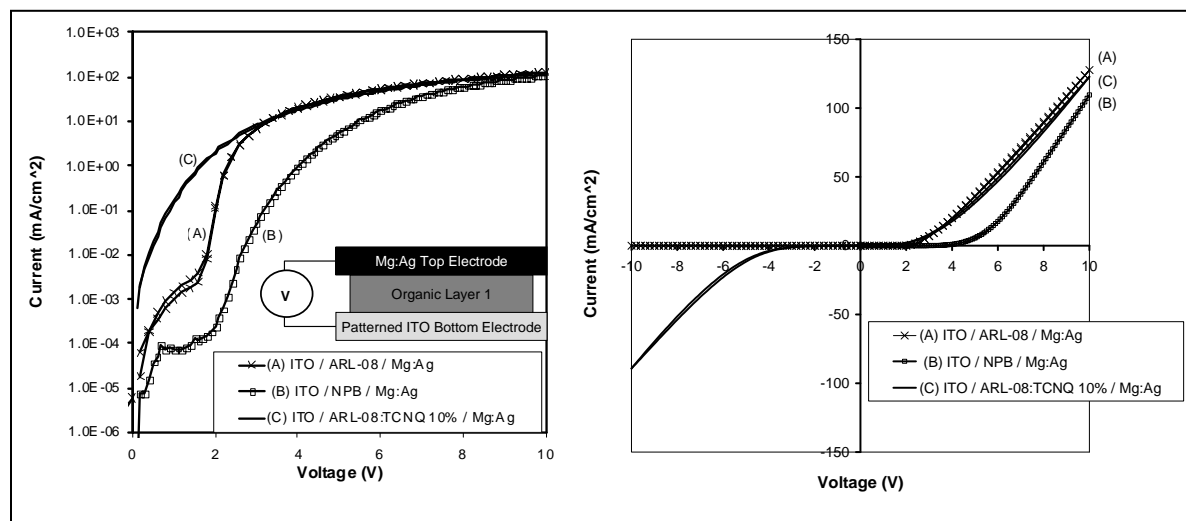


Figure 2. Comparison between the ARL-08 hole-transporting layer, a NPB-only device, and ARL-08 doped with 10% TCNQ, showing (a) the semi-log plot and (b) the linear plot.

These devices clearly demonstrate hole-carrier injection and transport from the ITO contact. We observe an improved hole-transport property for the undoped-ARL-08 as compared to NPB. The two undoped devices exhibit a space charge region from 0 V to approximately 2 V, above which the current is injected from the ITO contact and the current dramatically increases. By contrast, the ARL-08 doped with 10% TCNQ demonstrates a continuous hole injection and transport starting at 0 V. In addition, the reverse bias (positive voltage on the Mg:Ag electrode) for the ARL-08:TCNQ devices has a symmetric charge transport as compared to the forward bias; whereas, the undoped ARL-08 and NPB devices have low leakage space charge current.

The doped device results suggests that holes can be injected into ARL-08:TCNQ organic layer from the low-work function (Mg:Ag) electrode. Clearly, NPB and ARL-08 do not have this property. However, the device results in figure 2 for the ARL-08:TCNQ device do not preclude that electrons could be injected and transported in the organic layer. Based on these findings, the principal investigators (PIs) are filing a patent disclosure to cover the ARL-08 material application for hole injection and improved charge transport.

In figure 3, the device current-voltage (I-V) data is the semi-log plot for ARL-08 as a function TCNQ doping concentration. The data demonstrates the optimum TCNQ concentration is between 5% and 10%. The reverse bias data (negative voltage on the ITO electrode) in figure 3 has been multiplied by -1 in order to plot the reverse bias current on the semi-log plot. From this data, the undoped ARL-08 device exhibited four orders of magnitude less current in the reverse bias as compared to the ARL-08:TCNQ devices. Once, again, the data suggests the devices have nearly equal hole injection and transport properties from the ITO and Mg:Ag electrodes.

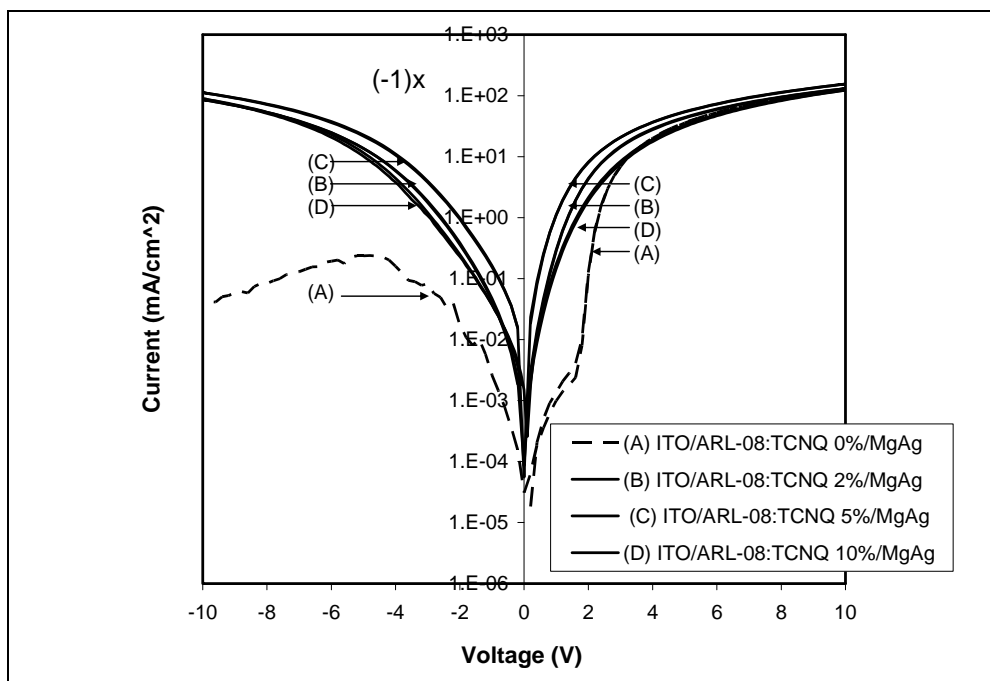


Figure 3. ARL-08:TCNQ as a function of TCNQ doping concentration.

3.2 Polymer Based Donor-acceptor Material

The second portion of the first-year DRI program was to develop a fundamental understanding the nature of the charge-transfer (CT) complex in equation 1 through chemical materials analysis. This analysis will lead to improved materials designs for next generation material. The following work is be submitted to Advanced Materials (3) by the ARL post-doc, Dr. Sanchao Liu.

In this effort, the novel conducting organic materials based on polycarbazole/TCNQ complexes were synthesized. The donors chosen were polycarbazoles with electron-donor groups, i.e., carbazole moieties, on the side chains. The TCNQ acceptor molecule can be inserted between two adjacent donor molecules for increased complex stability. Previous study by Litt et al. (4) showed that the polymer side chain complexes have up to 50 times higher equilibrium constants than those of the corresponding small molecule model complexes. Thus, polymcarbazole/TCNQ complexes can be formed at high ratio with high stability. Their structures are shown in figure 4.

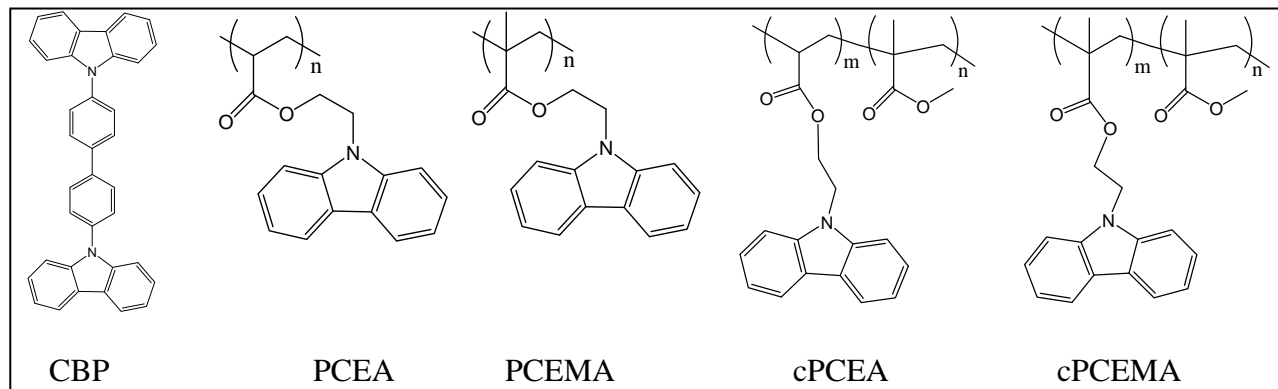


Figure 4. The structures of the donors: CBP: 4,4'-Bis(9-carbazolyl)-1,1'-biphenyl; PCEA: poly(9H-carbazole-9-ethyl acrylate); PCEMA: poly(9H-carbazole-9-ethyl methacrylate); cPCEA: poly[(methyl methacrylate)-co-(9H-carbazole-9-ethyl acrylate)], 25% PCEA; and cPCEMA: poly[(methyl methacrylate)-co-(9H-carbazole-9-ethyl methacrylate)], 15% PCEMA.

To study the formation of the CT complex between polycarbazole and TCNQ, CBP was used as the model compound. X-ray crystal structure analysis (figure 5) shows the formation of 1:2 CBP:TCNQ complex with the donor (carbazole moiety) and the acceptor (TCNQ) molecules alternately stacking together with the aromatic rings parallel to each other. In figure 5, the formation of the CT complexes between donor and acceptor are clearly shown by the X-ray structure.

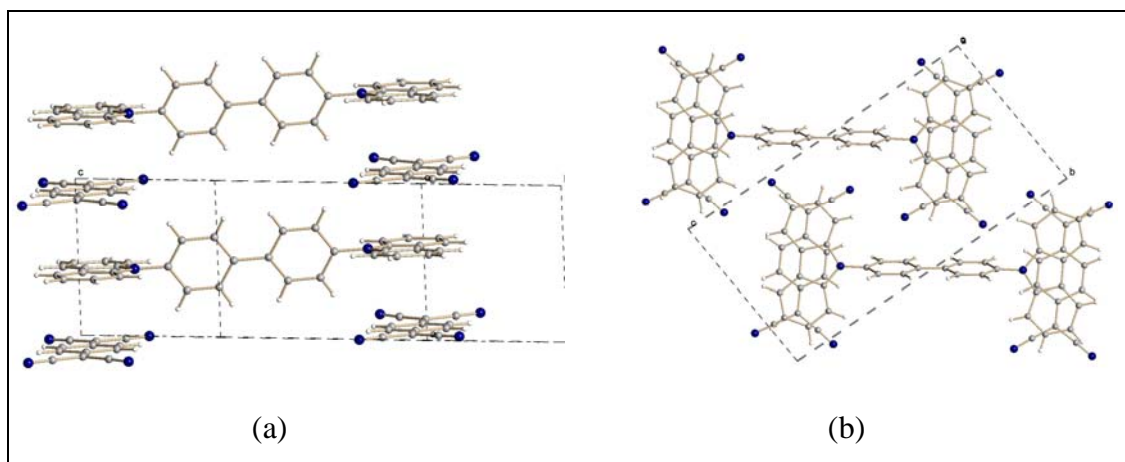


Figure 5. X-ray crystal structure of CBP/TCNQ complex showing the packing (a) projected along the b axis; (b) projected along the a axis.

4. Conclusions

In the first year of the two-year DRI, we have worked on developing novel ionization potential (IP) for organic based molecules using the donor-acceptor design concepts. Additionally, through this work, we are developing a more fundamental understanding of donor acceptor molecule stacking in order to guide future material designs.

During the second year, the team will improve the ARL-08 materials and integrate these materials into flexible display with the Army's Flexible Display Center (FDC). The fundamental materials research will be integrated into diode devices to evaluate the device properties as a function of the material formations.

5. References

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3. Lui, S.; Shi, J.; Forsythe, E. W.; Blomquist, S. M.; Chiu, D. Polymer Charge Transfer Complexes for Opto-electronic Applications. To be submitted *Advanced Materials*, 2009.
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6. Transitions

The material and device technology is being formulated into a patent disclosure. This preliminary work has been published in SPIE Proceedings and presented as an invited talk; however, the material structures were not disclosed. The fundamental research is being published in *Advanced Materials* and was presented at the FlexTech Alliance Flexible Electronics Conference in February 2009.

In parallel, we are working with the FDC to integrate the ARL-08 molecules and charge transfer complexes with flexible active matrix backplanes and organic light emitting diodes (OLEDs). This work will be explored for follow-on IP.

List of Symbols, Abbreviations, and Acronyms

2-D	two-dimensional
ARL	U.S. Army Research Laboratory
CBP	4,4'-Bis(9-carbazolyl)-1,1'-biphenyl
cPCEA	poly[(methyl methacrylate)- <i>co</i> -(9- <i>H</i> -carbazole-9-ethyl acrylate)], 25% PCEA
cPCEMA	poly[(methyl methacrylate)- <i>co</i> -(9- <i>H</i> -carbazole-9-ethyl methacrylate)], 15% PCEMA.
CT	charge-transfer
DRI	Director's Research Initiative
FDC	Flexible Display Center
IP	ionization potential
ITO	indium tin oxide
I-V	current-voltage
Mg:Ag	magnesium silver
NPB	4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl
OLEDs	organic light emitting diode
PCEA	poly(9 <i>H</i> -carbazole-9-ethyl acrylate)
PCEMA	poly(9 <i>H</i> -carbazole-9-ethyl methacrylate)
PIs	principal investigations
TCNQ	tetra-cyanoquinodimethane

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